



Pyrolysis of Pine Wood

Experiments and Theory

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PYROLYSIS OF PINE WOOD, EXPERIMENTS AND THEORY

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ABSTRACT: In this study, pinewood has been pyrolyzed using a fixed heating rate with a variable end-temperature. The pyrolysis process has been simulated using a mechanism with three parallel reactions for the formation of char, gas and tar. First order irreversible kinetics is assumed. This kind of model may predict the variation of product yield with operating conditions such as temperature and heating rate. The system of coupled differential equations describing the pyrolysis process is solved using the software DYMOLA. Various literature values for kinetic parameters have been compared with the experimental values. In this work the model was able to predict the volatile amount as a function of temperature in the interval from 250 to 1000°C with a good accuracy.

Keywords: biomass characteristics, pyrolysis, wood chips

1 INTRODUCTION

Biomass gasification is considered as one of the options to increase the use of biomass for energy purposes. The first step in the gasification of biomass (after drying) is the pyrolysis process where the biomass is broken down. The volatile fraction in biomass may account for more than 70 wt% of the biomass and it is thus important to be able to describe the pyrolysis accurately. The pyrolysis process in staged gasifiers, where pyrolysis and gasification takes place in separate reactors [1], can be characterised as "slow pyrolysis" meaning that the overall heating rate of the fuel, due to the particle size is relatively slow (10-20°C/min) meaning that the time resolution in which the process takes place is relative long (minutes). This can be compared to, for example, fluid bed gasification where the time resolution is very short (1/100 seconds). One of the main advantages of staged gasification is that by conducting the pyrolysis in a separate reactor in a controllable atmosphere and at controllable temperatures it is possible to produce char of a uniform quality. One of the main properties with regards to char quality is the residual amount of wood in the char. The residual wood may produce additional tar. This property is very dependent on the temperature history of the char and in particular the end-temperature and heating rate.

In this study, pinewood has been pyrolyzed using a fixed heating rate with a variable end-temperature. The pyrolysis process has been simulated using a mechanism with three parallel reactions for the formation of char, gas and tar. First order irreversible kinetics is assumed. This kind of model may predict the variation of product yield with operating conditions such as temperature and heating rate [2]. The system of coupled differential equations describing the pyrolysis process is solved using the software DYMOLA [3]. Various literature values for kinetic parameters have been compared with the experimental values. In this work the model was able to predict the volatile amount as a function of temperature in the interval from 250 to 1000°C with a good accuracy. Experiments and model calculations shows that for final temperatures above 600 and 400°C, respectively, the pyrolysis will be finished during the heating stage.

2 EXPERIMENTAL SECTION AND PROCEDURE

In order to make any conclusions about the residual amount of tar that may be evolved from biomass char it is very important to know the history of the char. Biomass char has been produced in the BGG (Biomass Gasification Group) laboratory under controlled conditions; different char qualities have been produced by pyrolysing biomass with varying end-temperatures. In this work pine wood samples have been pyrolyzed in an oven using fixed heating rates (6°C/min) followed by a two hours isothermal period using end-temperatures varying from 250 to 1000°C [4]. For producing the char, wood chips from French pinewood have been used.

2.1 Pyro-oven.

Before the pyrolysis, the wood chips were dried in an oven for 24 hours at 100°C. The dry wood chips were then pyrolysed in a special oven, batches of 20 g were heated at rates 6°C/min, and the atmosphere in the oven was kept inert by flushing with a constant flow of nitrogen. The end-temperature was kept constant for two hours, before cooling down, in order to achieve a uniform temperature of the char. shows an example of a temperature evolution during the pyrolysis.

After cooling down the char samples were weighted again in order to determine the loss due to the pyrolysis, figure 1 shows the result of the pyrolysis experiments, in the figure the release of volatiles is shown as percent weight loss of the initial wood sample. Two test series are shown, the initial test series (run 1) showed that in the interval from 250 to 400°C there was a very high weight loss from the char, in the interval from 400 to 600°C the degree of weight loss is reduced significantly and from 600 to 800°C no weight loss is observed. In order to verify the observations from the first test run a second series of experiments was conducted, in this test run some of the samples were repeated in order to determine repeatability for the experiments. Samples were also made at three new end temperatures in order to verify the characteristic curve of the volatilisation of the wood. In figure 1 all the measurements are shown.

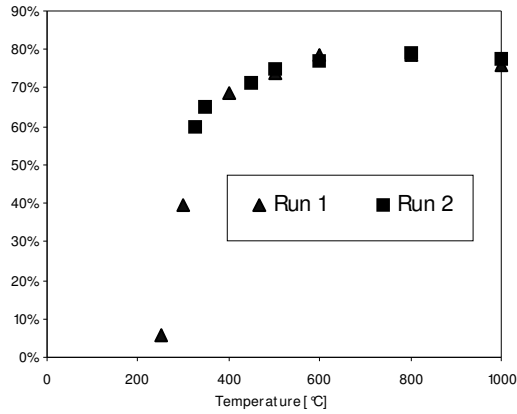


Figure 1. Volatiles (wt%) as a function of temperature.

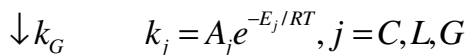
That there is no measurable weight loss of the char at pyrolysis temperatures above 600°C does not mean that volatiles are not released in this interval, the predominant volatile component released from the char at these elevated temperatures will though be hydrogen and the weight loss due to this is not detectable with the equipment used. The curve for the release of volatiles during pyrolysis corresponds well with what is seen in literature.

3 PYROLYSIS THEORY

Biomass consists basically of three types of polymers: cellulose, hemicellulose and lignin. As a rule of thumb the biomass consist of 1/3 of each type, though wood have higher lignin content than straw [5]. The first step in the gasification is a heating and drying of the biomass fuel. Subsequent heating results in a pyrolysis process which initiate at about 230°C, where the complex polymers in the biomass are broken down resulting in a gas consisting mainly of CO₂, H₂O, CH₄, CO, H₂, tar and char. The tar consists of various heavy organics that can condense and break down subsequent processes [6-7]. [8] described the fast breakdown of wood particles using a mechanism with three parallel reactions for the formation of primary pyrolysis products, char, liquids and gas. The mechanism with three parallel reactions can predict the variation of product yield with operating conditions [2].

CHAR

$\uparrow k_C$



GAS

(1)-(3)

Where k_G , k_L and k_C are reaction rate constants for the formation of gas, liquids and char, respectively. k is the total reaction rate constant for the decomposition of wood. Reactions orders different from 1 are difficult to give a true physical meaning [9]; therefore a first order reaction mechanism is used here. The formation of char,

tar and gas and break down of wood can be expressed using equations 4-7, respectively, where:

$$\frac{dm_c(t)}{dt} = k_c m_w(t) \quad (4)$$

$$\frac{dm_L(t)}{dt} = k_L m_w(t) \quad (5)$$

$$\frac{dm_G(t)}{dt} = k_G m_w(t) \quad (6)$$

$$\frac{dm_w(t)}{dt} = -k m_w(t) \quad (7)$$

where m_c , m_w , m_L and m_G are the weight of char, wood, tar and gas, respectively.

Various values of kinetic constants have been reported in the literature, [9-12], which is compared in table I. The Di Blasi parameters was used to model beech wood powder. The Turner parameters was used to model oak wood, whereas the Font parameters was used to model almond shells. The Chan parameters has been used to model large particle pyrolysis of pine wood.

Table I. Kinetic parameters for pyrolysis

PAR.	DIBLASI	CHAN	THURNER	FONT
Fuel	Beech wood	Pine wood	Oak wood	Almond shells
E_C (kJ/mol)	111.7	121	106.5	73.1
k_C (s ⁻¹)	3.2×10^9	1.08×10^7	7.377×10^5	2.98×10^3
E_L (kJ/mol)	148.0	133	112.7	119
k_L (s ⁻¹)	1.1×10^{10}	2.0×10^8	4.125×10^6	5.85×10^7
E_G (kJ/mol)	152.7	140	88.6	139.2
k_G (s ⁻¹)	4.38×10^9	1.3×10^8	14345	1.52×10^7

In the DiBlasi, Chan and Font models, the activation energy for char formation is lower than the activation energy for gas and liquid formation; this means that an increase in temperature promotes the production of volatiles rather than char and a decrease in temperature promotes the production of char. In the Thurner model, the activation energy for char formation is higher than the activation energy for gas formation.

3.1 Numerical method.

The pyrolysis equations (4-7) are solved using the Dymola differential equation solver [3]. The equations (4-7) are solved using the following initial conditions:

$$m_c(0) = m_L(0) = m_G(0) = 0 \text{ and } m_w(0) = 1 \quad (8)$$

The system of differential algebraic equations (DAE) is solved using the DASSL integration method [3] since this is the only DAE solver available in Dymola. DASSL is a variable step size method designed to integrate stiff

differential equations using a so-called BDF-method. The integration order is 1-5 and a relative accuracy of 10^{-5} has been used here, this is $1/10^{\text{th}}$ the recommended value of 10^{-4} . Using a recommended value of 10^{-4} means an accuracy of 3-4 digits [3], thus the relative accuracy used here means an accuracy that is better than 3-4 digits.

4 MODELLING RESULTS

The used temperature profile as a function of time for an end-temperature of 300°C(573 K) can be seen in figure 2.

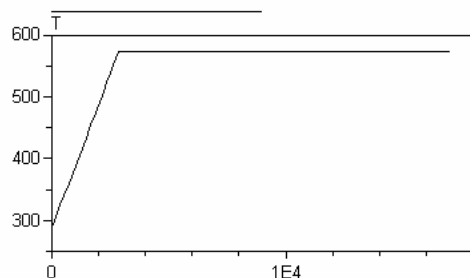


Figure 2. Temperature(K) as a function of time(s) for 300°C end-temperature, 6°C/min heating rate.

Pyrolysis is assumed to take place both during the heating and the isothermal pyrolysis, and the volatile amount is the sum of the volatiles evolved during the heating stage and the isothermal stage. Using the kinetic parameters from Di Blasi (table 1), the following results are obtained as a function of time for pyrolysis at 300°C, see figure 3

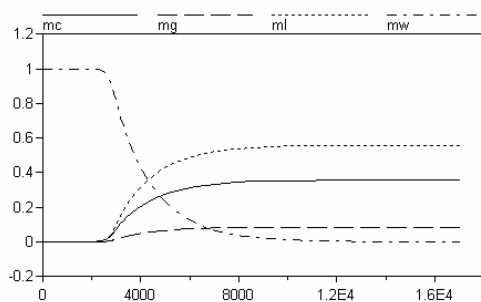


Figure 3. Pyrolysis products as a function of time(s) using a heating rate of 6°C/min and two hours at 300°C.

After two hours residence time at 300°C there was still 1 wt% of the wood left.

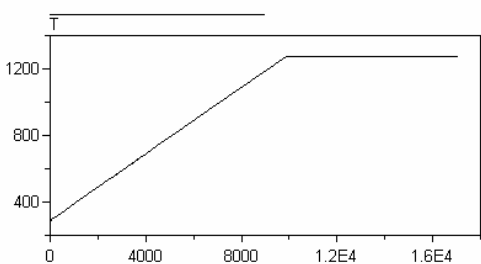


Figure 4. Temperature(K) as a function of time(s) for 1000°C end-temperature.

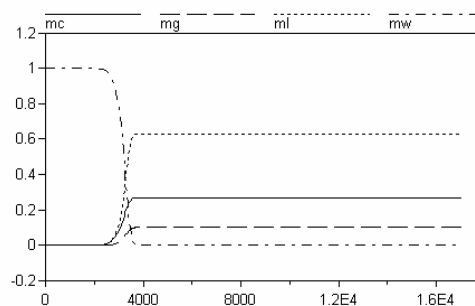


Figure 5. Pyrolysis products as a function of time(s) using a heating rate of 6°C/min and two hours at 1000°C.

Comparison of various kinetic parameters from literature The pyrolysis process was simulated using the Chan, Di Blasi, Thurner and Font kinetic parameters, see table 1. The results are shown in figure 6.

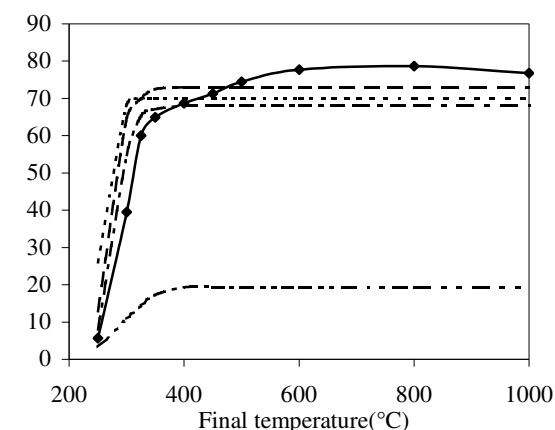
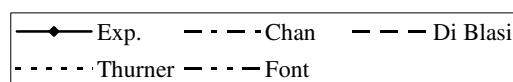


Figure 6. Volatiles(wt%) as a function of final temperature using a heating rate of 6°C/min and two hours at the final temperature.

As can be seen, the Font parameters do not match the pyrolysis experiment at all, the volatile amount at 1000°C is 19.4 % compared to the experimental value of 76.8 %. The other models gave a good match of the pyrolysis process. The Di Blasi parameters gave the best match of the pyrolysis at 1000°C, model predicts 73 % compared to the experimental value of 76.8 %. The pyrolysis up to 400°C is best described using the Chan parameters.

5 CONCLUSION

The pyrolysis model using three parallel pyrolysis reactions gives a good match of the pyrolysis experiments if pyrolysis during the heating is taken into account. Model calculations using Di Blasi parameters indicate that two hours residence time is not sufficient for fully pyrolysing at 300°C. At 300°C there were 1 wt % of the wood left after two hours. The model predicts that the pyrolysis distribution will stabilise at a temperature of

400°C with 63 wt % tar, 27 wt % char and 10 wt % gas. Higher temperatures do not change this distribution. Experiments predict that the volatiles stabilises at 600°C compared to the model prediction of a stabilisation at 400°C using a heating rate of 6°C/min. Experiments predicts that the volatile fraction stabilises at 76.8 % compared to the model prediction of 73 %. The Chan parameters gave the best match of the pyrolysis up to 400°C while the Di Blasi parameters gave the best match of the pyrolysis above 400°C. The Font parameters do not match the experiments at all.

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